

Citation for published version:

Argyle, IS, Pihlajamäki, A & Bird, MR 2015, 'Ultrafiltration of black tea using diafiltration to recovery valuable components', *Desalination and Water Treatment*, vol. 53, no. 6, pp. 1532-1546.
<https://doi.org/10.1080/19443994.2014.953400>

DOI:

[10.1080/19443994.2014.953400](https://doi.org/10.1080/19443994.2014.953400)

Publication date:

2015

Document Version

Peer reviewed version

[Link to publication](#)

This is an Accepted Manuscript of an article published by Taylor and Francis in *Desalination and Water Treatment* on 01.09.2015, available online: <http://www.tandfonline.com/10.1080/19443994.2014.953400>

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Ultrafiltration of black tea using diafiltration to recover valuable components

Abstract

Ultrafiltration of black tea liquor in a constant volume diafiltration regime has been carried out to remove the haze characteristically associated with this product. Commercial polymeric membranes with a range of molecular weight cut-offs (25, 50 and 100 kDa) fabricated from both polysulfone and fluoropolymer were used to assess the total solids throughput of the system. A shortfall in the amount of polyphenols transmission over the amount of residual tea solids transmission is the main driver for operating in this regime. The result of this shortfall means membrane permeates are impaired in terms of colour, flavour and health-giving properties. From an initial tea concentration of 1.0 wt.%, diafiltration was carried out, with rejection coefficients for total solids and total solids being assessed continuously. An acceptable (but not ideal) permeate product was the result, which showed excellent clarity (< 2.0 nephelometric turbidity units (NTU) in the majority of cases) although the associated transmission in polyphenols meant the tea has lost some of the deep red colour associated with a higher quality tea infusion. This shortfall in polyphenols transmission gave rise to higher concentrations of polyphenols in the retained side of the process than for original raw tea. In addition, membranes were pre-treated using ethanol, which had a significant effect on both their water permeability and zeta potential. When used in a filtration environment, fluxes increased for all membranes following treatment, with the 100 kDa polysulfone membrane recording a 41% increase in terminal filtration flux. With the exception of the 25 kDa polysulfone membrane, alcohol treatment resulted in all membranes showing increases in the total solids throughput, with the proportion of polyphenols transmitting through the membrane increased to a greater degree over all other components. The disproportionate increase in polyphenols transmission was attributed to reduced charge interactions following ethanol treatment. The results show that as fouling builds up, the separation of polyphenols from all other tea solids increases, meaning that small batches (relative to membrane area) and short-term operation is favoured, in order to maximise polyphenol content in the product stream. In summary, the operation of UF in a diafiltration regime is shown to be an effective industrial processing option for the clarification of black tea liquors.

Key words

Ultrafiltration, diafiltration, black tea, polyphenols,

1. Introduction

Globally, tea is one of the most popular beverages consumed, being second only to water. It is harvested from the plant *Camellia Sinensis* and grown predominantly in higher altitude regions (> 1200 m) of central and eastern Asia, and Africa [1]. China accounted for 33% of all tea production in 2010 (1.4 million tonnes) with the second largest producer, India, accounting for 0.97 million tonnes [2]. The price of tea averaged 2.72 USD/kg between 2008 and 2012 [3] and although classified as a commodity crop, products made from its infusion account for a significant part of the global soft-drink market. Ready-to-drink (RTD) teas, in both powdered and bottled form, occupied 8.7% of the USD 522 billion global soft drinks market in 2012/2013 [4].

These statistics highlight the mass appeal of pre-prepared tea infusions and the lucrative conversion of a basic food crop into a high value consumer product; continued growth of which is, in part, a result of innovations within the food technology and engineering sector. The food industry is continually looking to maximise productivity whilst expending fewer resources, be it raw materials, water, energy and other chemicals e.g., cleaning agents. The achievement of which is beneficial both environmentally and financially speaking. In addition, the drive of the industry to provide consumers with products of ever increasing functionality, which promote health and well-being, poses further challenges. These ideals mean the industry inherently strives for sustainability – in its classic definition – by attempting to unify and progress economic, social and technological factors harmoniously. This article focuses on the application of ultrafiltration (UF) as a means to clarify black tea.

1.1. Black tea polyphenols

As well as comprising of proteins, polysaccharides, caffeine, free amino acids and organic acids in varying proportions [5-7] it is perhaps the polyphenolic species which make tea infusions, and especially black tea, so characteristic in terms of taste. These constituents are formed by enzymatically catalysed oxidative polymerisation of catechins (the principal polyphenolic group found in green teas) during fermentation [8]. Green teas have been described as having ‘grassy’, ‘harsh’, ‘bitter’ and ‘slight non-tangy astringency’ taste sensations [7]. Though not unpleasant, the fermentation and firing of leaves to eventually form black tea infusions causes flavours to become ‘flowery’ with a ‘pleasant tangy astringency’ [7]. This is partly attributed to the formation of theaflavins (TFs) by dimerization of catechins. TFs are a well characterised group of flavan-3-ols typically in non-, mono- and di-gallated variants with the defining benzotropolone core, formed first by oxidation of catechins to (gallo)catechin quinones (by polyphenol oxidase/peroxidase activity), then by further substitution and oxidation of these intermediaries to form TFs [9]. In addition to these well-defined species, an ill-defined group collectively termed thearubigins (TRs) are also present in

high concentrations and are formed by oligo-polymerisation of catechins, TFs, and any combination thereof [9]. The structure of TRs is somewhat ambiguous, although elucidation of some of these structures [10] and the route to their synthesis [11] is not without endeavour. Black tea polyphenols were classified under low and high molecular weight fractions (low being less than 1000 g mol⁻¹) by Drynan et al., 2010 [11]. This serves as a convenient division given the varying colour of the species, with TRs exhibiting a darker and more reddish-brown characteristic to the brighter reddish-yellow (orange) appearance of TFs [12, 13].

1.2. RTD tea, haze and removal

Preparation of RTD tea begins like any other tea preparation; withered and crushed leaves are steeped in hot water (freshly boiled water for black teas and lower temperatures for green teas). A combination of centrifugal and filtration steps are then used to remove leaf debris. Upon cooling, a phenomenon known as tea creaming occurs through complexation of constituents, typically by polyphenol homo-association, protein-polyphenol, caffeine-polyphenol and other interactions (also stabilised by metal cations) thus causing formation of haze [14-16]. The degree of creaming is related to pH, infusion concentration and temperature [17]. The formation of this cream reduces the appeal of RTD tea through lowered clarity and colour and thus removal is a necessity. Current removal strategies involve solubilisation through alkalinisation of the tea and further pH readjustment although this can cause a loss in colour and create a stewed flavour [18, 19]. Other strategies are cold water extraction, chill de-creaming and chemical stabilisation although all have associated drawbacks [20].

1.3. Application of ultrafiltration

To date there have been a number of studies employing membrane technology to remove and reduce tea creaming, mostly focused on UF using polymeric membranes [21-24]. Membranes offer a low-impact strategy (in terms of energy, chemical addition, and damage to product) in which the molecules causing haze are selectively removed, with studies showing that the exclusion mechanism could be size-based, this founded on the haze aggregate sizes as measured by Liang and Xu, 2001 [18]. Charge interactions interfere with the transit of valuable solutes, having an impact on the levels of polyphenolics and as a result, the quality of the tea product. The efficiency of haze removal in these studies was acceptable and it was shown that by taking membranes with moderate hydrophilicity, subsequent filtration and cleaning resulted in membrane surface modification e.g. wetting properties/zeta potential which had both positive and negative effects on transmission of certain solutes, particularly when analysing model component mixtures [24]. In essence, modifications to UF membranes in terms of surface chemistry were shown to have powerful effects on permeate composition during black tea filtration.

This study aims to utilise some of the underlying surface chemistry phenomena and at the same time maintain a realistic industrial scenario. UF of black tea was carried out in constant volume dilution mode with solvent free diluent i.e. water. The regime has been selected to gain maximum mass transfer of tea solids through the membrane over a concentration mode regime, so as to avoid the effects of solute accumulation in the feed, which would lead to ever-decreasing fluxes. During preliminary experimentation using polysulfone membranes, the preferential rejection of polyphenols over other solutes occurred (this was also seen by Chandini et al., 2013 [25]). We propose that by operating in a diafiltration regime, a stream of added value can be created on the retained side of the membrane whilst still maximising solute yield in the permeate, as well as maintaining industrially viable fluxes. Subramanian et al. [26] state that no research reported to date has addressed the recovery of polyphenols and solids, the authors state that no attempts have been made to recover the polyphenolic rich retentate stream. This article addresses these issues by way of a pilot scale investigation for an individual unit operation. It offers the possibility of utilising a stream, which at some point during standard operation would be rejected as waste, to potentially be re-used upstream. This offers the opportunity of adjusting or standardising incoming liquors in terms of composition. In addition to analysing the filtration problem with standard ‘off the shelf’ commercial membranes, attempts to further alleviate the shortfall in solids recovery, and perhaps more importantly, polyphenols recovery were undertaken. The static pressurised pre-treatment of membranes using ethanol has a significant effect on both water permeability and apparent zeta potential (shown later) for the chosen membranes. It was theorised that this would influence the separative properties of the membranes to enable higher tea solids and tea polyphenols throughput.

2. Experimental

2.1. Filtration apparatus

UF was carried out on a DSS LabUnit M-10 filtration system (DSS, Silkeborg, Denmark). Membranes were contained in a DSS LabStack M-10 module housing 4 membrane coupons in 4 separate polysulfone plates in a plate and frame arrangement. The total effective filtration area was 336 cm². The filtration system comprised of an inline gear pump (ECO Gearchem, Pulsafeeder, NY, USA), shell and tube type heat exchanger (Alfa Laval, Nakskov, Denmark) connected via the shell side to a water bath. Flow rate was monitored using a rotameter allowing calculation of cross flow velocity (CFV). Transmembrane pressure (TMP) was monitored by the average of the pressure at the inlet and outlet (via pressure transducers, Druck, Leicester, UK) and subtraction of the permeate pressure (atmospheric). Feed solution was contained within a 10 L glass tank. Permeate mass was recorded gravimetrically by a balance. Temperature was monitored at the module inlet by a thermocouple. Mass/time of permeate, temperature and TMP was sent via a remote data acquisition module (ADAM-2012, Advantech, Milpitas, USA) to LabView software v.10.0 (National Instruments, Austin, USA) allowing calculation of permeate flux.

2.2. Membranes

Synthetic membranes of two material types were used for this study. Three polysulfone (PS) membranes and one fluoropolymer (FP) membrane were compared: product codes GR60PP, GR51PP, GR40PP and FS40PP. A summary of membrane properties is shown in Table 1. Membranes were cut to size and mounted in the plate and frame module. Prior to all filtrations, membranes were compacted for 10 minutes at 4.0 bar TMP with RO-water at 60 °C to ensure ample wetting of the matrix. Following this, membranes were rinsed with RO-water at 60 °C for 90 minutes to remove glycerol anti-humectant applied by the manufacturer. Following this, membrane pure water permeability (PWP) was tested at RT using RO-water between TMPs of 1.0 bar and 4.0 bar. All membranes were hydrophilic and comprised of PS/FP active layer and polypropylene support layers. Contact angles were measured using the sessile drop technique on dried membranes with ultra-pure water using a DataPhysics OCA 15 Pro goniometer (DataPhysics, Filderstadt, Germany). Values are recorded in Table 1 as an average and standard deviation of 10 – 15 measurements.

[Table 1]

2.3. Alcohol pre-treatment

UF membranes were also tested for their filtration performance following an ethanol pre-treatment protocol developed in-house. To pre-treat, membranes were first fluxed with RO-water to remove

glycerol anti-humectant and PWP was measured as previously described. Following this, the membrane module was mounted onto a purpose built pre-treatment apparatus. A stainless steel pressure vessel was filled with the treatment solution (50 % w/w ethanol and pressurised to 1.0 bar). A needle valve enabled treatment solution to flow into the module with a further needle valve allowing residual air/water to be bled out at the module outlet, leaving membranes completely immersed. Following this, permeate line valves were opened to allow treatment solution to be fluxed through the pores. After approximately 10 minutes, the permeate lines were sealed and the membrane was left immersed in treatment solution for 24 hours at RT. After system depressurisation and purging of treatment solution, membranes were thoroughly rinsed with RO-water and PWP was measured again. The relative permeability change (PWP_{rel}) is expressed as a ratio of final to initial PWP as shown in eq. 1.

$$PWP_{rel} = \frac{PWP_{final}}{PWP_{initial}} \quad (1)$$

2.4. Through-pore zeta potential

Apparent through-pore zeta potential was calculated using the streaming potential method. Electrical potential was measured between skin layer and support layer via suitably positioned Ag/AgCl electrodes. A 10.4 cm² membrane coupon was mounted in a purpose built module and fluxed with 1.0 mM KCl solution at a range of TMPs (0.5 – 1.0 bar), following thorough rinsing with distilled water at 1.0 bar TMP. Calculation of the apparent zeta potential (ζ) was made with knowledge of the streaming potential/pressure gradient using the uncorrected form of the Helmholtz-Smoluchowski relationship (eq. 2).

$$\zeta = \frac{TMP}{\Delta E} \frac{\mu k}{\epsilon_0 \epsilon_r} \quad (2)$$

Where E is the streaming current, μ and k are the solution viscosity and conductivity respectively, and ϵ_0 and ϵ_r are the permittivity of free space and the dielectric constant of water respectively. Measurements were made over a range of pHs (~ 4.0 – 7.0) which suitably covered the pH range of tea and that of many food stuffs. Electrodes were cleaned and regenerated after 10 sets of 5 – 6 pHs tested (5 membrane samples).

2.5. Black tea

Soluble spray-dried tea powder was of Sri Lankan origin and supplied by Unilever R&D, Colworth, UK. Tea was reconstituted with RO-water at 90 °C and agitated by a stirrer set at 500 rpm for 20

minutes. Tea containers were then immersed in a cold water bath to adjust the temperature to 50 °C. A feed volume of 8 L was used for all experiments.

2.6. Filtration experiments

After permeability measurement, filtration was carried out at 50 °C with 1.0 ms⁻¹ CFV. Initially, pressure ramping experiments were used to indicate rejection coefficients for solutes for 1.0 wt.% tea. Pressure was incrementally increased from a starting TMP of 0.5 bar to a final value of 4.0 bar allowing 20 minutes between TMP adjustments. Following this, diafiltration of 1.0 wt.% tea was carried out at 1.0 bar TMP for 5 hours with 1.0 ms⁻¹ CFV. Solute free diluent (RO-water) was added in 100 mL aliquots each time 100 mL of permeate was produced.

Terminal flux (J_T) of experiments was calculated as the average flux during the last 15 minutes of filtrations experiments. Relative fluxes were calculated in two contexts, relative to the virgin membrane (using the suitable flux from $PWP_{initial}$) allowing comparison of the effect of ethanol treatment on the tea filtration flux, and using the post-treatment flux (from PWP_{final}) which allows illustration of the extent to which fouling affects terminal filtration flux. These relative fluxes were termed $J_{rel(PWF1)}$ and $J_{rel(PWF2)}$ and calculated as show in in eq. 3 and eq. 4.

$$J_{rel(PWF1)} = \frac{J_T}{J_{PWP_{initial}}} \quad (3)$$

$$J_{rel(PWF2)} = \frac{J_T}{J_{PWP_{final}}} \quad (4)$$

Where J_T is the terminal fouling flux and $J_{PWP_{initial}}/J_{PWP_{final}}$ is the flux corresponding to $PWP_{initial}/PWP_{final}$.

2.7. Total solids

50 mL permeate and retentate samples were taken after approximately 30 minutes and 1 hour and then after every subsequent hour. Concentration was analysed by adding ~8 mL to pre-weighed 10 mL test tubes. After weighing again, samples were dehydrated in an incubator at 70 °C for 6 days. Samples were reweighed giving dry-weight/wet-weight and thus allowing sample concentration to be calculated.

2.8. Total polyphenols

Polyphenols were measured colourimetrically from the same samples as used for total solids analysis using a modified method as described by Singleton and Rossi, 1965 [27] in terms of gallic acid (GA) equivalents. Tea samples were mixed with acetonitrile (ACN) in the ratio 1.8 mL to 0.2 mL sample/ACN, this mixture being further diluted in 9 parts water to 1 part sample/ACN. 50 μL of this dilution was added in quadruplet to 300 μL 96 well microtiter plates containing 100 μL of Folin and Ciocalteu 2N reagent (Sigma Aldrich, Poole, Dorset) diluted 10-fold. 50 μL of GA standards of between 10 and 50 $\mu\text{g mL}^{-1}$ were added to wells in the same fashion alongside reagent blanks (distilled water), also in quadruplet. After between 2 – 8 minutes, 80 μL of sodium carbonate (7.5 wt.%) was added to the wells. Plates were incubated at RT for 8 hours prior to absorbance measurements at 765 nm in a Synergy HT multi-mode microtiter plate reader (BioTek Instruments, Winooski, USA).

2.9. Rejection coefficient of solutes

Feed/retentate and permeate solute rejection coefficients were calculated from concentration measurements using eq. 5 in which R_{app} is the apparent rejection coefficient, and c_p and c_r are the concentrations of solute i in the stream. These coefficients form the basis of stream analysis over time.

$$R_{app} = 1 - \frac{c_{p,i}}{c_{r,i}} \quad (5)$$

2.10. Definition of solutes

The solutes in tea have been divided into total polyphenolics (TP) and total non-polyphenolics or more simply, total residual solids (TRS). For a given stream, the total residual solids concentration is calculated by subtraction of TP from total solids (TS) (eq. 6).

$$c_{TRS} = c_{TS} - c_{TP} \quad (6)$$

2.11. Lightness, colour and turbidity

Permeate samples were transferred into 10 mm path length cuvettes (Fisher Scientific) and CIELAB tristimulus measurements were made by measuring transmittance of light using a Shimadzu UV-1601 spectrophotometer (Shimadzu, Kyoto, Japan) between 380 nm and 770 nm. UVPC Color Analysis software v.3.0 (Shimadzu) converted transmittance data to L^* , a^* and b^* coordinates. Colour coordinates were then compared to unfiltered tea coordinates of comparable concentration. Unfiltered coordinates are shown in Figure 1.

Haze of tea samples was quantified by measurement of tea sample turbidity at room temperature. Tea samples were loaded into glass cuvettes and mounted in a turbidimeter (model HI 93703, Hanna

Instruments, Woonsocket, USA). The instrument was 3-point calibrated using turbidity standards of 0, 10 and 100 NTU.

[Figure 1]

2.12. Diafiltration model – mathematical derivation

The scheme for a batch diafiltration is shown in Figure 2. As with any batch membrane process, permeate flows out at a time-dependant rate ($q(t)$). In the case of batch diafiltration, the concentration effect due to rejection of solutes is countered by the addition of a diluent. The diluent can be solute or solute-free and can be added at a rate determined suitable to give optimum system performance. There can be a number of regimes operated, the study of which becomes a complex optimisation problem as demonstrated by Kovacs et., 2010 [28] due to variability in rejection coefficients and the rate and compositional variability of diluent addition. As demonstrated by these authors, rejection coefficients in systems with explicit macro- and micro-solutes can change drastically over the process duration. This means utilisation of rejection coefficients obtained during standard permeate recycle experimentation (in this case from pressure ramping experiments) are likely to be invalid and must thus be determined experimentally from stream compositional analysis.

[Figure 2]

In this example, use of a solute free diluent added at a rate constant to that of the permeate flow rate is used to demonstrate the simplest operational arrangement. The generalised mathematical derivation for the bulk system and tea components follows.

Permeate volumetric flow rate (V_p) can be equated to the change in volume of permeate over time as follows:

$$\frac{dV_p(t)}{dt} = q(t) \quad (7)$$

Change in feed volume (V_f) at time t can be similarly expressed as the difference between permeate lost and diluent gained.

$$\frac{dV_f(t)}{dt} = u(t) - q(t) \quad (8)$$

If solutes are now considered, a mass balance can be expressed for the concentration of n number of solutes i at a given time if the diluent is solute free (i.e. water) as is the case here.

$$\frac{d}{dt} V_f(t) c_{f,i}(t) = -q(t) c_{p,i}(t) \quad \text{for } i = n \quad (9)$$

This can be expanded as:

$$c_{f,i}(t) \frac{dV_f(t)}{dt} + V_f(t) \frac{dc_{f,i}(t)}{dt} = -q(t) c_{p,i}(t) \quad \text{for } i = n \quad (10)$$

Substituting eq. 8 and using a rearrangement of the rejection expression as defined by eq. 5 for solute i : $c_{p,i}(t) = c_{f,i}(t)[1 - R_{app,i}(t)]$, gives:

$$V_f(t) \frac{dc_{f,i}(t)}{dt} = c_{f,i}(t) [q(t) R_{app,i}(t) - u(t)] \quad (11)$$

This sets the initial value problems for describing both total volume of feed and concentration of solutes i in the system for any diafiltration regime thus:

$$\frac{dV_f(t)}{dt} = u(t) - q(t) \quad V(0) = V_f^0 \quad (12)$$

$$V_f(t) \frac{dc_{f,i}(t)}{dt} = c_{f,i}(t) [q(t) R_{app,i}(t) - u(t)] \quad c_{f,i}(0) = c_{f,i}^0 \quad (13)$$

Since the example used here was operated in constant volume dilution mode with solute free diluent, eq. 13 can be integrated considering the relationship; $u(t) = q(t)$:

$$c_{f,i}(t) = c_{f,i}(0) e^{\frac{q(t)[R_{app,i}(t)-1]}{V_f(t)}} \quad (14)$$

Given that $u(t) = q(t)$, there is no change in the total feed volume of the system meaning eq. 12 is reduced to 0.

2.13. Separation factor

To quantify the fractionation of polyphenols from residual solids, the separation factor (α) has been defined as follows:

$$\alpha = 1 - \left(\frac{y_{TP}/y_{TRS}}{x_{TP}/x_{TRS}} \right) \quad (15)$$

Where x and y are respective mass fractions of solutes in the permeate and feed/retentate streams. For $\alpha = 1$, perfect fractionation occurs where all polyphenols are retained and all residual solids are transmitted. For $\alpha = 0$, the permeate has the same ratio of polyphenolics to residual solids as the feed i.e. a uniform filtration with respect to solutes

3. Results and discussion

3.1. Effect of membrane filtration on tea solute rejection

Figure 3 shows the rejection coefficients for total residual solids and total polyphenols calculated from streams using eq. 5 and eq. 6. The figures show a large discrepancy in the ratio of polyphenols transmission to total solids transmission over the TMP range for all membranes analysed. The most notable difference in rejection coefficients arising from the PS25 membrane at 0.5 bar (0.58 ± 0.01 for TP, 0.36 ± 0.01 for TS) and PS100 for 1.0 bar to 4.0 bar TMP (the coefficient values typically having a difference of between 0.22 and 0.20).

For the purposes of tea membrane filtration, where the permeate is the product stream, this presents a significant drawback in terms of tea quality assuming the polyphenol ‘stripping’ effect, and hence the polyphenol content, is the main consideration in terms of tea quality.

[Figure 3]

Given that polyphenols are being selectively retained in the feed/retentate side it follows that there is enrichment of the product in the retained stream if this fractionation mechanism continues during operation. This means that the non-target stream becomes a stream of added value as the filtration progresses, and the pre-determined point of disposal when making way for necessary clean-in-place (CIP) (when operating costs outweigh the profitability associated with material throughput) will result in the loss and thus wastage of high value tea components.

3.2. PWP change following alcohol treatment

Membrane PWPs following ethanol treatment showed permeability increases in all cases. The FP100 membrane showed the least significant relative change, 1.13 ± 0.06 (Figure 4). Contrastingly it was the similarly specified PS100 membrane which showed the most significant relative permeability increase (3.80 ± 0.19). A number of reasons could account for the flux changes seen across the TMP range and the elucidation of this phenomenon is the subject of a separate investigation. Reasons that are likely include a combination of both physical and chemical changes, and a number of theories are currently being assessed.

[Figure 4]

In terms of physical changes, or more specifically morphological changes, swelling and relaxation of the polymer constituting the active layer (PS) and/or active layer polymer-support layer interface are strong candidates to explain the findings. The possibility of increased slip and thus lowered hydraulic resistance to water is also considered. Other possibilities are pore ‘unlocking’ whereby the lowered surface tension of ethanol allows enhanced wetting of small pores which would be otherwise impenetrable to water when considering breakthrough pressures for the capillary rise/Washburn equation as explained by Kochan et al., 2009 [29]. By using ethanol as a pore activation fluid, a lower TMP is required to admit water into the pores. These relationships should be invalid given the spontaneous wettability (hydrophilicity) of the materials used in this example however the consideration of areas of apparent hydrophobicity, where Cassie-Baxter-type wetting behaviour may exist, cannot be discounted.

3.3. Apparent through-pore zeta potential

Streaming potential measurements revealed that for membranes treated with 100% ethanol, net charge was reduced to a less negative value i.e. charge neutralisation occurred inside the pores (Figure 5). The reduction of charge implies that the membranes are more susceptible to fouling by negatively charged species due to less repulsion between solutes and membrane and thus an enhanced deposition on or within the pore is a likely outcome. Evans et al., 2008 [23] showed that an FP100 membrane (ZP of < 1.0 mV from pH 3.8 to 7.0) was more prone to black tea fouling than a similarly specified regenerated cellulose (RC) membrane (> 1.0 mV for the same pH range), this being attributed to a lower magnitude virgin through-pore charge (negative charge) than the RC membrane, and a higher net charge when fouled compared to the RC membrane. This study highlighted the importance of membrane material when selecting membranes suitable for UF of black tea.

[Figure 5]

The reduction in charge can also partially explain the PWP increases observed although other factors are likely to contribute. By reducing the surface charge, the surface energy is reduced meaning there is a reduced affinity for dipole-dipole interactions (H-bonds) and wall slip inside the pores is increased. The alcohol is thus modifying the membrane by means of polymer dissolution bringing about a chemical change (the result of which becomes a physical swelling), or creating a thin film which acts as a lubricant for subsequent water transport. If swelling of pores is occurring, whereby a macroscopic expansion acts to increase pore size, the magnitude of electrical double layer overlap could also decrease. This could also occur due to intrinsic properties of the material being modified with or without the occurrence of pore size modification. The result of reducing double layer overlap would mean a decrease in the electro-viscous effect of water near to surfaces. The difference in pore

size would also then explain the much lower surface charge of the PS100 membrane compared to the PS25 and PS50 membranes prior to treatment. Given that the FP membrane showed the lowest response in terms of PWP uplift, it follows that a membrane of lower negative charge (as determined by Evans et al., 2008 [23]) cannot be as substantially modified as much as a membrane material of higher negative charge given that the predominant mechanism is one of charge magnitude reduction.

3.4. Diafiltration flux

Figure 6a and 6b shows the filtration flux data for the diafiltration experiments. PS25 exhibited the lowest terminal fluxes of $6.9 \pm 0.2 \text{ Lm}^{-2}\text{hr}^{-1}$ and $6.8 \pm 0.2 \text{ Lm}^{-2}\text{hr}^{-1}$ for untreated and treated experiments respectively. This represents an insignificant change statistically. For PS50, the untreated membrane gave a flux of $19.5 \pm 0.3 \text{ Lm}^{-2}\text{hr}^{-1}$ which rose to $25.2 \pm 0.5 \text{ Lm}^{-2}\text{hr}^{-1}$ post-treatment. PS100 showed the largest uplift during fouling which reflected the substantial PWP rise, rising from $26.6 \pm 0.3 \text{ Lm}^{-2}\text{hr}^{-1}$ to $37.4 \pm 0.5 \text{ Lm}^{-2}\text{hr}^{-1}$. FP100 showed a less substantial rise from $32.0 \pm 0.4 \text{ Lm}^{-2}\text{hr}^{-1}$ to $35.0 \pm 0.7 \text{ Lm}^{-2}\text{hr}^{-1}$. These results show that the flux increases observed in terms of PWP are being converted into a filtration environment for larger pore size membranes. For the PS25 membrane, the unchanged terminal filtration flux implies that performance in terms of volumetric throughput is stunted by fouling, with the likelihood that a surface cake layer ensures the membrane flux becomes independent of pore size and/or PWP.

In addition, the reduced surface charges mean that in-pore fouling would be increased, a key finding of Evans et al., 2008 [23]. It follows that even if the convective flow of solutes is greater, a direct result of increased flux, the effect of fouling would be worsened which thus restricts the true potential of the treatment method.

[Figure 6]

3.5. Diafiltration rejection coefficients

Stream concentrations were measured and converted to rejection coefficients which are displayed in Figure 7. In all cases the rejection coefficient for polyphenols was substantially higher across the duration of the diafiltration than for residual solids. PS25 (Figure 7a) and PS100 (Figure 7c) showed the largest discrepancy in these terms in accordance with the pressure ramping experiments displayed previously. Following ethanol treatment, PS25 solute transmission was unchanged. For PS50 (Figure 7b) and FP100 (Figure 7d) the concentration of polyphenols was increased in the permeate, as was the solids transmission, although somewhat more marginally. For PS100 there is a marked decrease in rejection of polyphenols after ethanol treatment meaning in terms of permeate product quality, the ethanol treatment has had a positive effect over the untreated membrane.

[Figure 7]

The net charge of the membrane plays an important role in allowing transmission of certain species, and even more so for those species with strong charges themselves. There are charges not only on the pore walls, but also on pore apertures. If these exhibit a strong negative charge, there will be a reduced fouling potential as material will be less inclined to deposit, however, strongly negatively charged species will be preferentially rejected over less charged species. Polyphenolic species, which are highly hydroxylated with low O–H bond enthalpy [30] (a key driver in their radical scavenging capability) will be dissociated in solution creating respective negatively charged phenolate anions and H^+ cations. These anions would thus experience more charge repulsion away from the membrane pores inhibiting their passage and thus transmission through the membrane. By removing this charge, or at least reducing it, the deposition of material on the membrane surface would increase (neutrally charged particulates agglomerating in solution in an analogous process). In addition, lowered repulsion would mean better transmission of these solutes into the mouths of pores and thus better transmission. This also explains why the FP100 membrane transmits solutes with more uniformity than the other membranes (using ZP measurements given in this article and from Evans et al., 2008 [23]).

Inside the pores the susceptibility for fouling (given lower charges) would be greater, based on previous evidence. This is confirmed considering that the relative flux reduction from the PWP to the terminal flux for ethanol treated membranes is consistently greater than for untreated membranes. Relative fluxes are shown in Figure 8 as calculated by eq. 3 and eq. 4. FP100 shows the most comparable ratio in relative filtration fluxes when using both untreated and treated PWPs as references. The largest difference is for PS100 which reflects the massive PWP post-treatment uplift.

[Figure 8]

3.6. Effect on retentate composition

Rejection coefficients shown in Figure 7 were fitted with curves within the filtration duration in order to gain continuous expressions for rejection coefficients; determination coefficients (r^2) for the fits exceeded 0.95 in all cases and were of the form: $R_{app,i} = at^b$, where a and b are non-phenomenological coefficients derived purely for fitting purposes. Given the continuous functions for $R_{app,i}$ and utilising experimental data for rate of diluent addition ($q(t)$), eq. 14 was used to calculate stream concentrations, and further, mass fractions along the time course. The advantage of using this method over purely experimental measurements is that concentrations are corrected to a reference concentration (in this case 10.1 gL^{-1} or 1.0 wt.%), which removes variability between experiments.

Given that the only approximation is for rejection coefficients, approximated well by the power-law fit, there is low error associated with the application of this data-driven model. However intrinsic knowledge of rejection coefficients is needed by prior experimentation if the model is to be used predictively.

Figure 9 shows the enrichment of polyphenols in the retentate plotted against the experimental permeate volume data. As previous flux data suggested, the PS25 and PS50 membranes (Figure 9a) transmit significantly less feed than PS100 and FP100 (Figure 9b). This means that despite the separative properties the PS25 membrane exhibited in terms of fractionation of polyphenols, the diafiltration does not progress as far compared to other membranes. The effect of ethanol on the rate of polyphenol accumulation is also significant. The fact that polyphenols are more easily transmitted after ethanol treatment means that the rate is slowed (for PS50 and PS100) although given the greater rate of dilution and consequently higher rejection coefficients, the retained stream has approximately the same composition of polyphenols after 5 hours filtration, but a lower concentration, due to the additional diluent which has been added to maintain the system volume. The FP100 showed similar profiles as the shift in rejection coefficients post treatment were proportional and only the volume processed was greater.

[Figure 9]

3.7. Separation factor

Figure 10 shows the relationship between the feed concentration and the calculated separation factor (determined using eq. 15). PS25 (both untreated and treated) (Figure 10a) exhibit similar profiles and show that the feed concentration after 5 hours has only been diluted to a small degree (from 1.0 wt.% initial concentration to ~ 0.94 wt.%). This is purely a reflection of the low flux and thus low rate of diluent addition.

[Figure 10]

Even though the diafiltration shows minimal progression for PS25, the rate of change of the separation factor is significant. This indicates that the rejection of polyphenols is strongly dependant on fouling build-up over time and less so due to progressive dilution of the feed. This is a key finding, as it aids design when considering process operability. For example, if heavy foulant build-up is effective in stripping a greater degree of polyphenols from the permeate, the recommendation in terms of operability should either be (i) to bias the operation towards using smaller batches over shorter time periods with more frequent membrane regeneration (CIP), or (ii) to increase the membrane area to

batch volume ratio so as to ‘spread’ the fouling and shorten operation times; of course this second approach has implications in terms of capital expenditure on plant equipment.

For PS50 (Figure 10a) and PS100 (Figure 10b) the effects of ethanol treatment are again evident with FP100 (Figure 10b) showing little effect after treatment. The separation factor rate of change with respect to feed concentration is lower following ethanol treatment meaning that a more consistent permeate is produced across the process duration. In an ideal scenario, a membrane should have a separation factor as close to zero for this application meaning ethanol treatment is having a positive effect. The composition of tea cream aggregates should not influence this greatly as the proportion of solutes involved in cream formation compared to the unbound solutes is thought to be less than 1.0% of all solids, on a volume basis [18], and will thus not play a role in limiting the potential transmission for any given solute.

3.8. Tea solids yield

Figure 11 illustrates the performance of the system. The main objective is to maximise the recovery of tea solids whilst having as little impact as possible on the relative compositions of solutes within the process duration. The graph shows that for untreated membranes, the higher flux and more consistent rejection of solutes means the FP100 membrane offered the best performance; an estimated 25.4 g from a possible 80 g was recovered. Following treatment however, the total solids transmission of the PS100 membrane gave by far the best performance (31.8 g transmitted). The total amount of polyphenols transmitted in the same time period also rose (4.4 g to 6.8 g of a possible 20.8 g).

[Figure 11]

3.9. Tea permeate quality

Figure 12 describes the appearance of the tea providing an indirect method for assessing quality. As shown in Figure 12a, the redness is being substantially removed from the tea infusion in comparison to the unfiltered tea. At the start of the filtration (where permeate concentration is highest), the redness is greatest, with the highest redness measurement occurring for PS100 following ethanol treatment in the early stages of filtration. This result correlates well with the rejection coefficients for polyphenols (Figure 3a) and suggests that it is the complex TRs which are being removed most predominantly, these species imparting a red/brown characteristic to the tea infusion [12] as well as a darker appearance; also affirmed by the lightness increases in Figure 12c. Considering yellowness (Figure 12b) and all membranes (excluding PS25) show a decreasing trend as the filtration progresses although a yellowness increase is observed until the latter stages of the filtration. Yellowness in tea brews has been reported to correlate with increased concentrations of various TFs [13]. This would mean that TFs are transmitting the membrane effectively at the early stages of filtration though as

filtration proceeds, an ongoing transition begins to obstruct their transmission, caused by a combination of lowered feed concentration (through bulk feed dilution) and increased membrane fouling. A similar effect was seen by Wu and Bird, 2007 [24] who showed that inclusion of TRs in model tea component solutions led to reduced membrane mass flux measurements of various TFs when analysing a 30 kDa MWCO PS membrane.

[Figure 12]

Considering the highly complex polyphenolic nature of TRs, it is likely that these species behave similarly to humic acids during membrane filtration, and fouling, given the occurrence of phenol, catechol and quinone groups present in both structures. Yuan and Zydney, 1999 [31] suggest that aggregation may be caused by intermolecular hydrophobic interactions. If the rejection of these species is due to solute aggregation then rejection through size exclusion would become a pre-dominant rejection mechanism and more so with smaller pore size membranes, even though the size of unbound constituents is likely to be below that of the membrane pore size. This would explain the large discrepancy between PS25 and all other membranes given the similar ZPs recorded for this and the PS50 membrane. Tea membrane fouling may be influenced by the area of water treatment and humic acid fouling and findings could have potential application for a range of polyphenol rich food stuffs e.g. red-fruit juices, red wine, beer etc.

Figure 12c and 12d show haze removal for untreated and treated membranes; this being the main motivation for this study. No defining trend can be observed across the concentration range for permeate product. The maximum value (1.99 ± 0.51 NTU) occurred arbitrarily for the FP100 membrane after 3.2 hours filtration. Nevertheless, the reduction in turbidity to below 2.0 NTU in all cases shows (i) that UF for haze removal of tea is highly efficient given the > 100 NTU values for comparable concentrations of unfiltered tea, and (ii) that ethanol treatment has little or no effect upon permeate turbidity. There is an indication that the PS25 membrane removes more haze than for the other membranes tested as, on the whole, the absolute values and errors were lower. This would support the theory that the removal of redness is a necessary consequence of haze removal and aggregation (and consequential size exclusion) of these species is a significant driver for tea cream formation at the elevated filtration temperature used in this study (50 °C).

4. Conclusions

Constant volume diafiltration has been carried out as an operating strategy to maximise total solids and total polyphenols throughput into permeate streams during the UF of black tea. Using complimentary techniques to assess the quality of the permeate, it has been shown that haze removal efficiency is greater with the smaller pore size membranes (PS25) yet there is nevertheless excellent haze removal achieved using all other membranes tested. There is a large discrepancy in the transmission of polyphenolic species compared to all other species (as shown by assaying and colour measurements), this being attributed to varying chemistry of the component mixture. In particular the red pigmented species (TRs) are being lost to a high degree and it is likely that aggregation of these species is causing substantial rejection, particularly with the PS25 membrane. In contrast to this, yellow pigmented species (TFs) are transmitted optimally and have a positive effect on the yellowness of the permeate. The behaviour does not last for the whole process duration with effects of fouling and dilution eventually retarding species transmission. The effect of fouling upon solute rejection (for bulk polyphenolics) was shown to be significant. This indicates that operating for shorter periods of time between CIP cycles would maximise polyphenolic yields in the product.

The difference in polyphenolic transmission over non-polyphenolic species during diafiltration leads to a net accumulation of polyphenols in the feed/retentate. This results in waste stream enrichment of polyphenols, addition of this upstream to the feed could upgrade product quality or be used as a method for standardising streams to maintain overall product consistency.

The same membranes were also pre-treated with ethanol solutions to investigate their effects. Large water permeability gains were seen during tea filtration, meaning the operating flux was not entirely cake dominated. A greater transmission of polyphenols into the permeate was also seen for PS50 and PS100 membranes, accompanied by increases in redness and yellowness over untreated membranes. This observation has been attributed to a reduced charge through the membrane pores and thus a lowered repulsion effect of negatively charge phenolate ions from the negatively charged membranes. The net effect of this charge reduction is that in-pore and more generally, organic fouling, is increased, as greater deposition of solutes occurs on a more neutral pore wall. However, this is outweighed by the greater convective mass transport of the solution through the membrane. The net

result of ethanol treatment is that membranes are able to transmit more solute into the permeate and thus efficiency gains in terms of mass yield are achieved.

For future development in this area, the refinement of the operating regime in terms of feed volume to membrane area ratio, exploration of regimes such as feed and bleed, and variations such as variable volume dilution present a highly complex optimisation problem. Significantly, simple membrane pre-treatment methods that modify membrane surface properties have the potential to be implemented as 'pre-treatment-in-place' strategies in industrial operation.

List of abbreviations

CIP	Clean-in-place
DSS	Danish Separation Systems
FP	Fluoropolymer
NTU	Nephelometric turbidity units
PS	Polysulfone
RO	Reverse osmosis
RT	Room temperature
RTD	Ready-to-drink
TF	Theaflavin
TR	Thearubigin
UF	Ultrafiltration

List of nomenclature

a^*	Redness parameter (CIELAB colour space) (-)
a, b	Fit parameters (-)
b^*	Yellowness parameter (CIELAB colour space) (-)
c	Concentration (wt.%)
CFV	Cross flow velocity (ms^{-1})
J	Flux ($\text{Lm}^{-2}\text{hr}^{-1}$)
J_T	Terminal flux ($\text{Lm}^{-2}\text{hr}^{-1}$)
k	Conductivity (μScm^{-1})
L^*	Lightness parameter (CIELAB colour space) (-)
PWF	Pure water flux ($\text{Lm}^{-2}\text{hr}^{-1}$)
PWP	Pure water permeability ($\text{Lm}^{-2}\text{hr}^{-1}\text{bar}^{-1}$)
q	Permeate flow rate (Ls^{-1})
R	Rejection coefficient (-)

t	Time
TMP	Transmembrane pressure (bar)
u	Diluent flow rate (Ls ⁻¹)
V	Volume (L)
x/y	mass fraction of solute in permeate/retentate (-)
ΔE	Streaming current (mV)
α	Separation factor (-)
ε ₀	Permittivity of free space (Fm ⁻¹)
ε _r	Dielectric constant of water (-)
ζ	Zeta potential (mV)

List of subscripts

f	Feed
i	Solute
p	Permeate
app	Apparent
rel	Relative
TP	Total polyphenols
TRS	Total residual solids
TS	Total solids

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